

# Electric properties of amorphous silver chalcogenides with content of carbon nanotubes at pressures up to 50 GPa

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**Abstract.** This paper is devoted to the analysis of structure of amorphous ionic conductors  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3$  with carbon nanotubes content,  $x = 0.4; 0.5; 0.6$  by means X-ray and Raman spectroscopy. The influence of DC and AC electric field on the electrical properties of materials at ambient pressure, and at pressures up to 50 GPa was studied.

## 1. Introduction

Ionic and mixed conductors based on silver and copper chalcogenide have been known as promising materials for development of new types of memory cells such as SEM (solid electrolyte memory), which is based on the properties of solid electrolytes [1-3], electrodes, resistive materials in electronics for manufacturing of resistors with functional dependence on the time of electric resistance in microelectronic devices with low values of currents and voltages, which are required for switching over various time periods, etc.

In order to obtain materials with a high ionic conductivity component, glassy silver chalcogenides  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3$  with the addition of carbon nanotubes (CNT) were synthesized.

The aim of this work is analysing the structure, estimating of ionic component of conductivity, investigating of influence of AC electric field and high pressure on electric properties of synthesized vitreous sulfides  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3$  with the addition of carbon nanotubes with  $x = 0.4; 0.5; 0.6$ .

## 2. Materials and methods of study

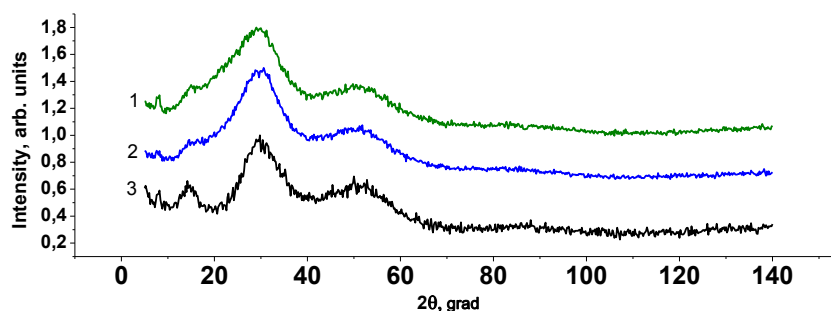
The synthesis of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3$  ( $x = 0.4; 0.5; 0.6$ ) with additional of  $\sim 7$  atomic percent of CNT was carried out by means of alloying initial components (as initial components was applied chemical reagents of high purity, nanotubes were added to the blend as composite with dehydrated sulfur) in the quartz containers evacuated to residual pressure  $10^{-4}$  Pa, filled with a superpure argon to  $0.5 \cdot 10^5$  Pa. Glassy chalcogenides were obtained by quenching from the melt, materials have a reddish tint, conchoidal fracture typical for glassy compounds, and are transparent to light at thickness less than 0.5 mm (figure 1).





**Figure 1.** Image of piece appearance  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$  with  $x = 0.4$ .

X-ray qualification of materials (figure 2) have been performed with diffractometer Shimadzu XRD 7000 (monochromatic radiation  $\text{CuK}\alpha$ ). Also, Raman spectroscopy was used for the qualification (Raman confocal microscope Alpha300R). The surfaces of samples were investigated with a scanning electron microscope, Auriga CrossBeam Zeiss, providing the X-ray microanalysis (EDS). The X-ray maps of elements distributions were obtained by means of EDS analysis. The distribution of all elements on the maps is uniform, which indicates of homogeneity of glass and the ratio of atomic percent of elements contained in the glasses corresponds to stoichiometric. Energy-dispersive spectrum of the synthesized materials contained peaks of elements used for the synthesis. According to the results of quantitative analyses of several points of samples were established atomic ratio of  $\text{Ag} / \text{Ge} / \text{As} / \text{S}$  in three synthesized materials corresponding to  $\text{AgGe}_{1.4}\text{As}_{0.6}\text{S}_3$ ,  $\text{AgGe}_{1.5}\text{As}_{0.5}\text{S}_3$ , and  $\text{AgGe}_{1.6}\text{As}_{0.4}\text{S}_3$ .



**Figure 2.** Powder diffraction patterns of compounds  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$ : 1:  $x = 0.6$ ; 2:  $x = 0.5$ ; 3:  $x = 0.4$ .

Electrical properties were investigated by impedance spectroscopy in the frequency range from 1 Hz to 32 MHz in the cells with copper, silver and graphite electrodes. Measurement and analysis of impedance was performed by universal frequency response analyzer Solartron 1260A. Studies at a direct current were carried out in the Solartron 12962 cell using Solartron Analytical Modulab.

For Raman investigation Probe NanoLaboratory NTEGRA Spectra (NT-MDT, Russia), which comprises high resolution confocal scanning laser microscope, Raman spectrometer, and scanning probe microscope (SPM) was used. The He-Ne laser with  $\lambda = 633 \text{ nm}$  and power 30 mW was used as a pumping source. Laser focusing was performed by objective x100 (NA = 0.95) mounted in inversed microscope Olympus IX71. A diffraction grating 600 dash/mm with spectral resolution 0.091 nm was used for light decomposition.

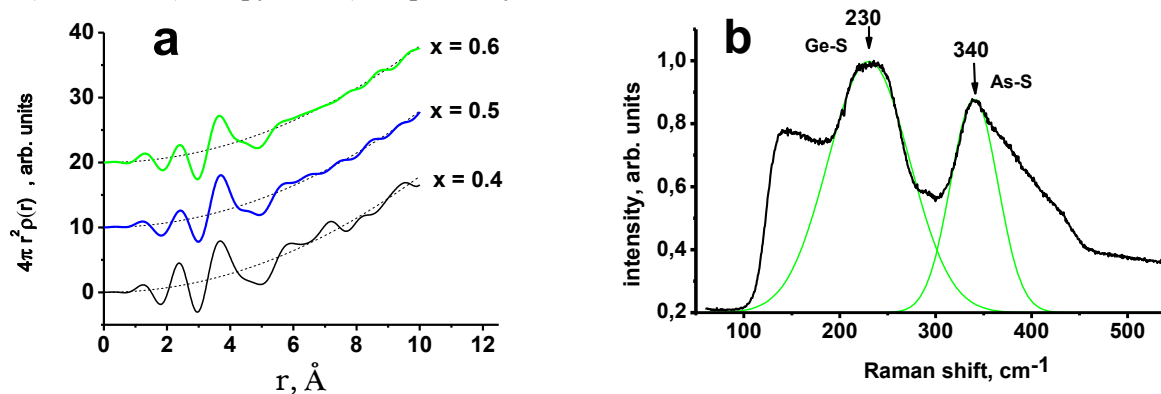
High pressure has been generated in the diamond anvil cell (DAC) with anvils of the rounded cone-plane type made of synthetic carbonado-type diamonds [5]. Anvils made from synthetic diamond consist of dielectric grains of diamond with layers of conducting materials. These anvils are good conductors and allow measurement of the electrophysical properties of samples placed in the DAC [4,

5]. Pressure values in the DAC were determined from the applied load using calibration data for reference materials with error not exceeding 10% in the pressure range of 15-50 GPa [5].

### 3. Results and Discussion

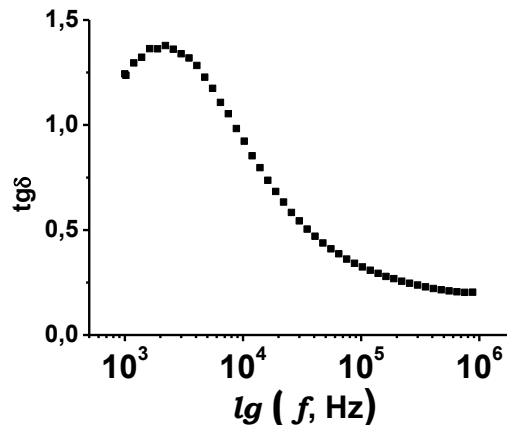
There are several halos on powder diffraction patterns in the same areas of angles as for the glassy materials from systems Cu-Ag-Ge-As-Se [6], Ag-Ge-As-Se [7, 8] and Ag-Ge-As-S [9]. The radial distribution functions (RDF) of the materials (figure 3a) are similar to RDF of glassy materials from the systems Ag-Ge-As-S and Ag-Ge-As-Se. The differences between RDFs of study materials and mentioned before observed in secondary order scale due to the presence of carbon nanotubes. The X-ray maps of elements distributions were obtained by means of EDS analysis. The distribution of all elements on the maps is uniform, which indicates of homogeneity of glass.

Assuming that the base of glass network as in the case of vitreous Ag-Ge-As-Se materials [7] are layered packages of randomly alternating tetrahedrally coordinated atoms of germanium and silver via sulfur and arsenic atoms, and packaging of tetrahedra in glass close to the GeAsS structure, then the high ionic conductivity in these compounds is due to the fact that silver ions can move easily between layers. This assumption is confirmed by the analysis of the structure using the Raman scattering methods. There are intensity maxima at 230 and 340  $\text{cm}^{-1}$  on the Raman spectra (figure 3b), which may correspond to vibrations of Ge-S bonds (tetrahedra with four-coordinated germanium atom in the centre) and As-S (AsS<sub>3</sub> pyramids), respectively [10].



**Figure 3.** (a) – Experimental Radial distribution functions of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$  ( $x = 0.4; 0.5; 0.6$ ). (b) – Raman spectra of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$  with  $x = 0.4$ . The He-Ne laser with  $\lambda = 633 \text{ nm}$  and power 30 mW was used as a pumping source.

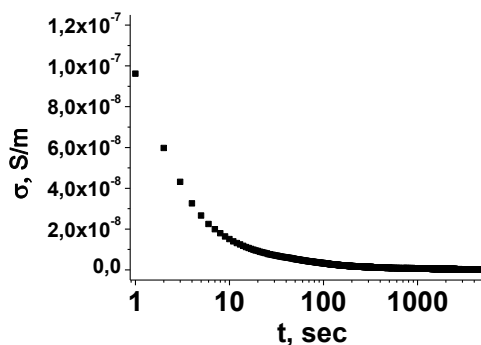
It is known that materials from the system of Ag-Ge-As-S are good ionic conductors [9, 11]. Evaluation of relaxation times in the synthesized materials was performed from the frequency dependence of tangent of dielectric loss (figure 4).



**Figure 4.** Frequency dependence of tangent of dielectric loss ( $\text{tg}\delta$ ) for  $\text{AgGe}_{1.5}\text{As}_{0.5}\text{S}_3 + \text{CNT}$  ( $x = 0.5$ ).

It is equal to  $7.21 \cdot 10^{-5}$  s. for  $\text{AgGe}_{1.5}\text{As}_{0.5}\text{S}_3 + \text{CNT}$ . Such time is typical for ion-relaxation polarization, which is caused by excessive transfer weakly bounded ions in an electric field on distance in scale that characterize the structure of glassy materials.

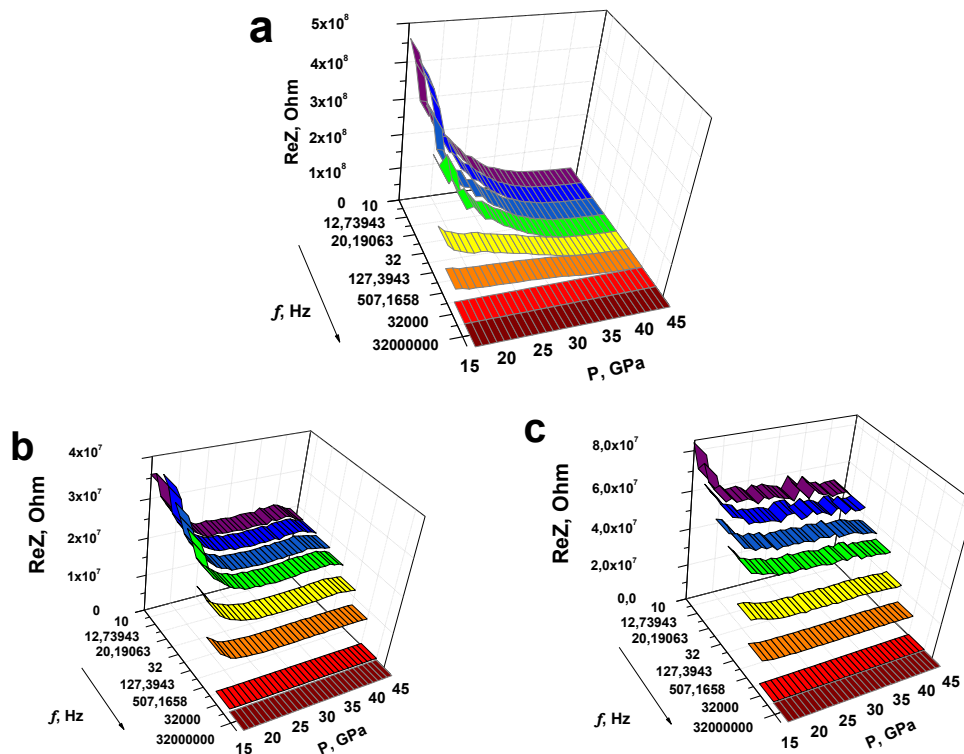
To estimate polarization time, i.e. the time from switching on DC until the resistance reaches a constant value, the time dependence of the electrical conductivity in the cell with blocking ion component electrodes (copper) at a constant voltage was measured (figure 5). The share of the ionic conductivity of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$  ( $x = 0.4, 0.5, 0.6$ ) materials is not less than 99 percent.



**Figure 5.** Time dependence of conductivity of  $\text{AgGe}_{1.6}\text{As}_{0.4}\text{S}_3 + \text{CNT}$  in the cell with blocking electrodes at a constant voltage which is equal 1V. The point of  $t = 0$  corresponds to start of measure.

Studies of impedance in the AC frequency range of 1 Hz to 32 MHz at pressures up to 50 GPa have shown that the real part of the impedance decreases with increasing of pressure and frequency (figure 6).

In [12], it is shown that the real part of the impedance of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3$ ,  $x = 0.4; 0.5; 0.6$  remains unchanged with pressure increasing up to 28 GPa. The rise of  $\text{Re}Z$  was observed at further pressure increase for materials with  $x > 0.4$ . This behavior of  $\text{Re}Z$  significantly different from observed by us, which can be caused by adding of carbon nanotubes and providing easier transport of carriers with pressure increasing.



**Figure 6.** Baric and frequency dependences of the real part of impedance of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$  a:  $x = 0.4$ ; b:  $x = 0.5$ ; c:  $x = 0.6$ .

#### 4. Conclusion

The structure of amorphous  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3$  with nanotube content at  $x = 0.4$ ;  $0.5$ ;  $0.6$  was analyzed. Analysis of structure by means of X-ray methods, and with the help of Raman spectra showed that the most probable structural units of glass are tetrahedra with four-coordinate germanium atom in the center and  $\text{AsS}_3$  pyramids.

Investigations of impedance at frequency range of 1 Hz–32 MHz at pressures up to 50 GPa have shown that the real part of impedance decrease with increase of pressure and increase of frequency of the alternating electric field.

Evaluation of relaxation times in the synthesized materials was performed from the frequency dependence of tangent of dielectric loss. That time is typical for ion-relaxation polarization.

The share of the ionic conductivity of  $\text{AgGe}_{1+x}\text{As}_{1-x}\text{S}_3 + \text{CNT}$  ( $x = 0.4, 0.5, 0.6$ ) was estimated. It is not less than 99 percent.

#### Acknowledgments

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